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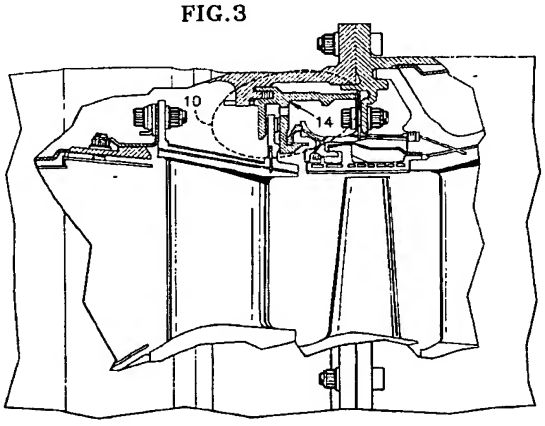
(54) Insulating thermal barrier coating system

(57) The invention concerns a thermal barrier coating system (12) requiring no bond coat adherence high temperature heat treatment and having enhanced insulating capabilities such that it may be applied to gas turbine engine components of varied shape, thickness and size. In preferred embodiments, the system includes a metallic bond coat which does not require a bond coat adherence high temperature heat treatment to form a bond between the metallic bond coat and a metallic substrate to which it is applied. A porous ceramic insulating layer is deposited on the metallic bond coat. In another preferred embodiment, the porous ceramic insulating layer is deposited directly on the metallic substrate.

The coating system is particularly advantageous for insulating metallic components prone to distortion in heat treatment and those requiring insulation in an as machined condition.

FIG.3



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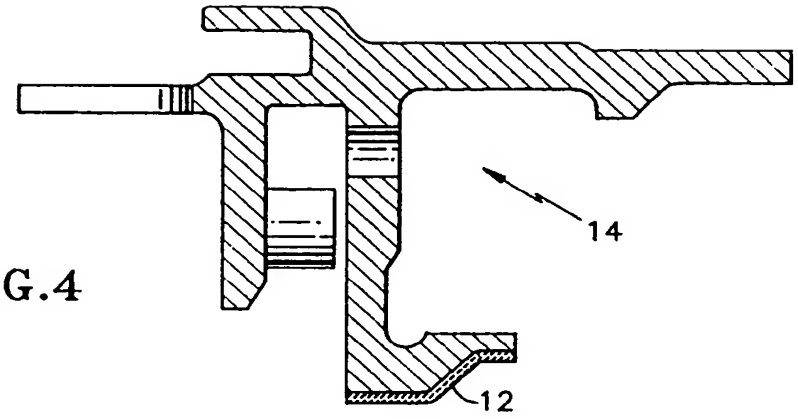

FIG.4

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D scription

This invention relates to ceramic thermal barrier coating systems used to insulate substrates from elevated temperatures.

Modern gas turbine engines, particularly those used in aircraft, operate at high rotational speeds and high temperatures for increased performance and efficiency. There is a high demand for improved performance and efficiency because of the desire to increase the range an aircraft can fly without stopping to refuel.

Today's modern gas turbine engines rely primarily on nickel base and cobalt base superalloys for the material ofthe engine components in many critical applications. As operating temperatures increase, however, the property limits of the base alloy materials are being approached.

Accordingly, attempts have been made to use coatings to protect certain components within the engine from the harsh operating environment. In particular, ceramic thermal barrier coatings are increasingly employed to protect turbine components, such as turbine blades, thereby extending the life of the blades and permitting enhanced fuel economy. Such protective coatings are necessary because some components in the turbine section must withstand high stresses and corrosive gas streams at temperatures greater than 2500°F (1371°C).

Many ceramic thermal barrier coating system applications, however, include a metallic bond coat which requires a bond coat adherence high temperature heat treatment to maximize the strength of the bond between the substrate and the metallic bond coat. While the bond coat adherence heat treatment is conventionally applied after application of the ceramic material, it could be performed prior to depositing the ceramic material. An exemplary bond coat adherence high temperature heat treatment includes heating a ceramic coated substrate in a nonoxidizing environment for one to ten hours at 1800°F (982°C) to 2050°F (1121°C).

This requirement may not be an undue burden for the coating of 3 inch to 6 inch (7.6 cm-15.2 cm) turbine blades and may in fact be required due to the high temperature, dynamic environment in which the turbine blades operate. However, application of this type of ceramic thermal barrier coating system and its high temperature heat treatment is an undesirable option for many other components in need of protection. For example, sheet metal components, such as the exemplary combustor shown in FIG 1, which are inconveniently large and prone to warpage mitigates against the use of such a bond coat adherence high temperature heat treatment and thus mitigates against the use of a thermal barrier coating system employing such a heat treatment.

In addition, we recently encountered the need to thermally insulate a component without subjecting it to a bond coat adherence high temperature heat treatment because of the need to insulate it in an as machined condition, without any subsequent machining to size, to avoid component distortion. However, to our knowledge we are not aware of an existing thermal barrier coating system having 66684.595 superior insulating characteristics which does not require such a high temperature heat treatment to successfully bond the metallic bond coat to the substrate.

Accordingly, what is needed is a thermal barrier coating system requiring no bond coat adherence high temperature heat treatment and having enhanced insulating capabilities such that it may be applied to gas turbine engine components of varied shape, thickness and size.

It is an object of the present invention to provide an insulating thermal barrier coating system for a metallic substrate.

It is a further object of the present invention to provide an insulating thermal barrier coating system as above requiring no bond coat adherence high temperature heat treatment and having enhanced insulating capabilities.

It is yet a further object of the present invention to provide a method of insulating a metallic substrate.

In accordance with the present invention, an insulating thermal barrier coating system for a metallic substrate is presented. The insulating thermal barrier coating system comprises a metallic bond coat receiving no bond coat adherence high temperature heat treatment to form a bond between the metallic bond coat and the metallic substrate to which the metallic bond coat is applied; and a porous ceramic insulating layer deposited on the metallic bond coat.

In accordance with a particular embodiment of the present invention, the insulating thermal barrier coating system comprises a metallic bond coat consisting substantially of, in weight percent, 15-40Co, 10-40Cr, 6-15Al, 0-0.7Si, 0-2.0Hf, 0.01-1.0Y, balance Ni. The metallic bond coat received no bond coat adherence high temperature heat treatment to form a bond between the metallic bond coat and the metallic substrate to which the metallic bond coat is applied. The coating system also comprises a porous ceramic insulating layer on the bond coat. The porous ceramic insulating layer comprises zirconia partially stabilized with about 6-8 weight percent yttria, and has a porosity between about 20-35 volume percent and a thickness between about 25-50 mils (0.635-1.27 mm). Porosity is intentionally created within the ceramic insulating layer by incorporating a small amount of polyester powder within the ceramic material.

In accordance with yet another particular embodiment of the present invention, a method of applying the previously described coating system is described.

The invention also extends in broad terms to a metallic substrate thermally insulated with a porous ceramic insulating layer comprising, in weight percent, zirconia partially stabilized with about 6-8 yttria and having a porosity between about 20-35 volume percent.

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Certain preferred embodiments of the present invention will now be described by way of example only and with reference to the accompanying drawings, in which:

FIG. 1 is a schematic illustration of a gas turbine combustor;

FIG. 2 is a bar chart depicting oxidation resistance performance of various thermal barrier coating systems applied to different segments of a gas turbine combustor;

FIG. 3 is a cross-section of a portion of a modern gas turbine engine with a first stage turbine vane support area encircled;

FIG. 4 is an enlarged view of the first vane support shown in FIG. 3; and

FIG. 5 is a logarithmic graph depicting life versus temperature for an uncoated first stage turbine vane support and that of a first stage turbine vane support coated with a preferred insulating thermal barrier coating system of the present invention.

According to the present invention an insulating thermal barrier coating system is applied to a metallic substrate. The substrate may be made of a conventional nickel base or cobalt base superalloy material and may be cast and machined to desired final shape/size using known techniques.

Prior to applying the insulating thermal barrier coating system to the substrate, the substrate is prepared to receive the coating system. Preparation is conventional and includes cleaning the substrate surface to remove contamination. Suitable cleaning methods include, but are not limited to, aluminum oxide grit blasting. Preferably, the surface is roughened by the cleaning process to aid the adherence of the subsequently applied bond coat to the substrate.

A metallic bond coat requiring no bond coat adherence high temperature heat treatment is then applied to the substrate. As will become apparent from the description set forth herein, a preferred feature of the present invention is use of a metallic bond coat receiving no such high temperature or diffusion heat treatment.

Thus, the invention is particularly advantageous for insulating metallic components prone to distortion during heat treatment or those requiring insulation in an as machined condition. The invention is also particularly advantageous for insulating materials whose properties may not be capable of withstanding exposure to such a high temperature heat treatment without, for example, losing strength or oxidizing. Thus, the invention is advantageous for insulating metallic components which are intolerant of high temperature bond coat diffusion heat treatment cycles.

The invention has particular utility in insulating static gas turbine engine components, such as turbine vanes and turbine vane supports, because these components do not undergo the centrifugal forc s as do turbine blades.

Yet another significant advantage is the cost savings associated with eliminating a subsequent heat treatment step.

Preferably, a metallic bond coat of a NiCoCrAlY material is employed, particularly if oxidation resistance is desired. In the context of this invention, Ni denotes nickel, Co denotes cobalt, Cr denotes chromium, Al denotes aluminum and Y denotes yttrium. The bond coat material has a composition falling within the broad weight percent range of 15-40Co, 10-40Cr, 6-15Al, 0-.7Si, 0-2.0Hf, 0.01-1.0Y, balance essentially Ni. Preferably, the bond coat material has a composition falling within the weight percent range of 20-26Co, 15-19Cr, 11.5-13.5Al, 0-.7Si, 0-2.0Hf, 0.20-0.70Y, balance essentially Ni. The particle size ofthe bond coat material is preferably within the range -170+325 US std. sieve (44 to 88pm).

The bond coat thickness may be between about 0.001-0.015 inches (0.076-0.381 mm). Preferably the thickness ofthe bond coat is between about 0.005-0.009 inches (0.127-0.229 mm). The bond coat is preferably plasma sprayed, in air, on the surface of the substrate to be protected. Other deposition techniques, including but not limited to, high velocity oxy fuel (HVOF) spraying or cathodic arc deposition may be employed.

Preferably, the surface topography of the bond coat is such that it is suitable to receive the subsequently applied ceramic material. Preferably, the metallic bond coat is plasma sprayed, in air, which will yield a roughened bond coat surface.

Upon the above described metallic bond coat, a porous ceramic material comprising zirconia partially stabilized with 6 to 8 percent (by weight) yttria is then applied. The ceramic material is preferably plasma sprayed in air and the substrate temperature is maintained at less than 500°F (260°C). Other deposition techniques, including but not limited to, high velocity oxy fuel (HVOF) may also be employed.

The ceramic particle size is between about 5 and about 180 microns (.005 and about .18 mm) and preferably about 50 microns (.05 mm) mean diameter. Porosity is intentionally created within the ceramic coating. Preferably, porosity is achieved by incorporating between about 1-12 weight percent polyester powder within the ceramic. We most prefer the use of 1.5 to 3.0 weight percent polyester powder (60 micron (.06 mm) nominal particle size) with the ceramic to produce a porosity on the order of 20 to 30 volume percent. High porosity levels, in excess of about 35 volume percent, may produce coatings susceptible to erosion damage.

An advantage of intentionally introducing the above described porosity is that it provides spall resistance which allows the ceramic material to be applied at an increased thickness. The thickness of the ceramic coating can range from 25 to 50 mils (.635 to 1.27 mm) and preferably from 25 to 35 mils (.635 to .889 mm).

In another embodiment of the invention, other ceramic materials having low thermal conductivity, includ-

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ing but not limited to, zirconia fully stabilized with yttria, zirconia stabilized with ceria, or ceria may be substituted for the above described zirconia partially stabilized with yttria.

In yet another embodiment of the present invention, the above described ceramic layer may be deposited directly on the metallic substrate, without the use of a bond coat. This embodiment may be feasible for insulation of oxidation resistant alloys, for example, alloys including active elements, such as yttrium, calcium, or magnesium, or alloys made from low sulfur bearing materials, or alloys subsequently desulfurized. For marginally oxidation resistant alloys, direct bonding of the ceramic layer may also be feasible if the substrate is preoxidized in a controlled manner to grow a strongly adherent oxide interlayer. With the elimination of the bond coat, this embodiment may be advantageous for static applications in a nonerosive environment or where the substrate temperature can be maintained at less than about 1800°F (982°C). For proper bonding of the ceramic material to the substrate, however, it may be necessary to roughen the surface of the substrate by techniques, including but not limited to, grit blasting. This embodiment is primarily suitable for operating environments in which the coating is not subjected to excessive thermal or mechanical stress at the substrate/ceramic interface.

The present invention will now be described by way of examples which are meant to be exemplary rather than limiting.

Example 1

Various ceramic thermal barrier coating systems, including preferred embodiments of the present invention, were applied to cast combustor segments. The material of each segment was made from the same base alloy having a nominal composition, in weight percent, of 8.0Cr, 10Co, 6.0Mo, 6.0Al, 4.3Ta, 1.15Hf, 1.0Ti, 0.015B, 0.08Zr, balance Ni (B-1900+Hf). The test segments occupied portions of rows 2, 3 and 4 on the outer liner ofa gas turbine combustor.

The liner was then subjected to a severe test employing conditions more demanding than those encountered in normal operation of a gas turbine engine. The test included 1300 cycles. The first 300 cycles were run under normal takeoff conditions; 1000 of the cycles included 5.5 minutes at maximum allowable operating temperature which accelerated the oxidation rate per cycle. It should be noted that the combustion process is such that flame conditions in the region of rows 2 and 3 were hotter than that of row 4.

The benefits of the present invention are clearly illustrated in FIG. 2 FIG. 2 depicts the oxidation damage (or lack thereof) of the various segments. Oxidation damage was determined by visually inspecting each segment for any burned/oxidized portions and determining the approximate severity of damage.

The left-most bar (A) on the chart represents the performance of a coating consisting of zirconia partially stabilized with 6-8 weight percent yttria plasma deposited in air on a NiCoCrAlY bond coat (nominal composition, in weight percent, of 23Co, 17Cr, 12.5Al, 0.45Y, balance Ni) which was also plasma deposited in air. The thickness of the bond coat was about 0.007 inches (0.178 mm), and the thickness of the ceramic material was about 0.014 inches (0.356 mm). This Sample A was applied to 5 of 10 segments on row 2 of the outer liner. Sample A did not include any intentionally introduced porosity.

A preferred insulating thermal barrier coating system of the present invention was applied to the remaining 5 segments in row 2 by first plasma spraying, in air, the bond coat. The material of the bond coat had nominal composition, in weight percent, of 23Co, 17Cr, 12.5Al, 0.45Y, balance Ni. Next a porous ceramic material comprising zirconia partially stabilized with 6 to 8 weight percent yttria was air plasma sprayed upon the bond coat. Porosity was intentionally created within the ceramic material through the incorporation of about 2.0 weight percent polyester powder (60 micron (.06 mm) nominal particle size). The thickness of the bond coat and the ceramic material was substantially the same as that of Sample A.

Three (3) out of 5 segments coated with Sample A exhibited trailing edge oxidation damage up to .040 inches (1.02 mm) in depth. None of the 5 segments coated in accordance with the preferred embodiment of the present invention exhibited trailing edge oxidation damage.

The coating of Sample A, as described above, was also applied to 4 of 7 segments tested on row 3 of the outer liner. The preferred insulating thermal barrier coating system of the present invention was applied to the remaining 3 segments tested, as described above except the thickness of the bond coat and the thickness of the ceramic material was increased by a factor of 1.5 each. Four (4) out of 4 segments coated with Sample A coating exhibited trailing edge oxidation damage up to 0.40 inches (1.02 mm). Zero (0) out of 3 segments coated in accordance with the preferred embodiment of the present invention exhibited trailing edge oxidation.

The coating of Sample A, as described above, was applied to 3 of 6 segments tested on row 4 of the outer liner. The preferred insulating thermal barrier coating system of the present invention, as in row 2, was applied to the remaining 3 segments tested. None of the 3 segments coated with Sample A coating exhibited trailing edge oxidation damage. Similarly, 0 out of 3 segments coated in accordance with the preferred embodiment of present invention exhibited trailing edge oxidation.

It can be seen that the coating performance of th preferred embodiments in terms of oxidation d gradation resistance meets and even exceeds that of the Sample A coating system when tested under conditions which are more severe than those normally encoun-

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tered in engine operation. This example also illustrates the superior insulating capabilities of the present invention.

Exampl 2

FIG. 3 schematically illustrates a cross-section of a modern gas turbine engine with a first stage turbine vane support area 10 encircled. A preferred insulating thermal barrier coating system 12 of the present invention was applied to the inner diameter surface of a first stage turbine vane support 14, as shown in FIG. 4. The substrate material of the first vane support 14 was 19.5Cr, 13.5Co, 4.25Mo, 3.0Ti, 1.4Al, 0.07Zr, 0.007B, balance Ni (AMS 5707 (Waspaloy)). The inner diameter of the first stage vane support 14 was cleaned and conditioned by aluminum oxide dry blasting prior to application of the insulating thermal barrier coating system 12.

The insulating thermal barrier coating system 12 was then applied by first plasma spraying, in air, a preferred bond coat of the present invention to a thickness of about .003 inches (.076 mm). The material of the bond coat had nominal composition, in weight percent, of 23Co, 17Cr, 12.5Al, 0.45Y, balance essentially Ni and powder particle sizes within the range -170+325 US std. sieve (44 to 88pm).

Next a porous ceramic material comprising zirconia partially stabilized with 6 to 8 weight percent yttria was air plasma sprayed upon the bond coat. The substrate temperature was maintained at less than 500°F (260°C).

The size ofthe ceramic powder particles was about 50 microns (.05 mm) in mean diameter. Porosity was intentionally created within the ceramic material through the incorporation of about 2.0 weight percent polyester powder (60 micron (.06 mm) nominal particle size). The thickness of the ceramic material varied between about 25 and 35 mils (.635 and .889 mm).

The article was then subjected to a 935 cycle engine test simulating flights at various maximum engine power conditions. The article exhibited no cracking upon visual inspection as well as upon fluorescent penetrant inspection.

Another article coated with a preferred insulating thermal barrier coating system of the present invention was tested in an engine operating for five minutes at an exhaust gas temperature approximately 75°F (24°C) above the maximum temperature encountered in normal engine operation. This was a most severe test employing conditions which are more demanding than those normally encountered during typical gas turbine engine operation. This article also exhibited no cracking upon visual inspection as well as upon fluorescent penetrant inspection.

Example 3

FIG. 5 further illustrates the significant benefits of the present invention. FIG. 5 depicts the life of the first stage turbine vane support 14 with and without a preferred insulating thermal barrier coating system 12 of the present invention versus temperature. As can be seen from the graph, simulated engine operation at a first stage turbine vane support substrate temperature of approximately 1600°F (871°C) as measured by thermocouples resulted in a predicted life of 2000 cycles for an uncoated first stage turbine vane support (AMS 5707 (Waspaloy)). The significance of operation at 1600°F (871°C) is that this temperature is well above the maximum allowable use temperature for AMS 5707.

However, by coating the inner diameter of the first stage turbine vane support 14 with a preferred insulating thermal barrier coating system 12 of the present invention, the substrate temperature ofthe first stage turbine vane support 14 was calculated to be reduced to approximately 1450°F (788°C) and an extended predicted life of 19,000 cycles under the same operating conditions was achieved. The extension of life by 17,000 cycles illustrates the tremendous insulating benefit of the present invention.

Claims

1. An insulating thermal barrier coating system (12) for a metallic substrate (14) comprising:

   a. a metallic bond coat which has received no bond coat adherence heat treatment to form a bond between the metallic bond coat and the metallic substrate to which the metallic bond coat is applied; and
   b. a porous ceramic insulating layer deposited on the metallic bond coat.

2. An insulating thermal barrier coating system (12) for a metallic substrate (14) comprising:

   a. a metallic bond coat consisting substantially of, in weight percent, 15-40Co, 10-40Cr, 6-15Al, 0-0.7Si, 0-2.0Hf, 0.01-1.0Y, balance Ni, wherein the metallic bond coat has received no bond coat adherence heat treatment to form a bond between the metallic bond coat and the metallic substrate; and
   b. a porous ceramic insulating layer on the bond coat, the porous ceramic insulating layer comprising, in weight percent, zirconia partially stabilized with about 6-8 yttria, the porous ceramic insulating layer containing a porosity between about 20-35 volume percent, wh rein the porosity is intentionally created within the insulating layer by incorporating a polyester material,

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the insulating layer having a thickness between about 25-50 mils (0.635-1.27 mm).

3. A coated article comprising a metallic substrate having thereupon an insulating thermal barrier coating system comprising:

a. a metallic bond coat which has received no bond coat adherence heat treatment to form a bond between the metallic bond coat and the metallic substrate to which the metallic bond coat is applied; and
b. a porous ceramic insulating layer deposited on the metallic bond coat.

4. A coated article which comprises a substrate selected from the group consisting of Ni and Co base superalloys having thereupon an insulating thermal barrier coating system comprising:

i) a metallic bond coat consisting substantially of, in weight percent, 15-40Co, 10-40Cr, 6-15Al, 0-0.7Si, 0-2.0Hf, 0.01-1.0Y, balance Ni, wherein the metallic bond coat received no bond coat adherence heat treatment to form a bond between the metallic bond coat and the substrate; and
ii) a porous ceramic insulating layer on the bond coat, the porous ceramic insulating layer comprising, in weight percent, zirconia partially stabilized with about 6-8 yttria, the porous ceramic insulating layer containing a porosity between about 20-35 volume percent and having a thickness between about 25-50 mils (0.635-1.27 mm).

5. A system or coated article as claimed in any preceding claim wherein the substrate or article is a gas turbine engine component.

6. A system or coated article as claimed in any preceding claim wherein the substrate or article is a first stage turbine vane support.

7. A system or coated article as claimed in any of claims 1 to 5 wherein the substrate or article is a combustor liner.

8. A system or coated article as claimed in any of claims 1 to 5 wherein the substrate or article is a segment of a combustor.

9. A method of insulating a metallic substrate including the steps of:

a. providing a clean substrate surface;
b. depositing a metallic bond coat receiving no bond coat adherence heat treatment to form a bond between the metallic bond coat and the metallic substrate; and
c. depositing a porous ceramic insulating layer on the metallic bond coat.

10. A method as claimed in claim 9 wherein the substrate surface is cleaned by grit blasting prior to depositing the metallic bond coat.

11. A method as claimed in claim 9 or 10 wherein the metallic bond coat is deposited by plasma spray, in air.

12. A method as claimed in claim 9 or 10 wherein the metallic bond coat is deposited by high velocity oxy fuel spraying.

13. A method as claimed in claim 9 or 10 wherein the metallic bond coat is deposited by cathodic arc deposition.

14. A method as claimed in any of claims 9 to 13 or a coated article as claimed in claim 3 wherein the metallic substrate is selected from the group consisting of nickel and cobalt base superalloys.

15. A method as claimed in any of claims 9 to 14 or a coated article as claimed in claim 3 or 14 wherein the composition of the metallic bond coat consists substantially of, in weight percent, 15-40Co, 10-40Cr, 6-15Al, 0-0.7Si, 0-2.0Hf, 0.01-1.0Y, balance Ni.

16. A method as claimed in any of claims 9 to 15 or a coated article as claimed in claim 3, 14 or 15 wherein the porous ceramic insulating layer comprises, in weight percent, zirconia partially stabilized with about 6-8 yttria and contains a porosity between about 20-35 volume percent, wherein the porosity is intentionally created within the insulating layer by incorporating a polyester material.

17. A method as claimed in any of claims 9 to 16 or a coated article as claimed in claim 3, 14, 15 or 16 wherein the porous ceramic insulating layer has a thickness between about 25-50 mils (0.635-1.27 mm).

18. A coated article having a substrate having thereupon an insulating thermal barrier coating system consisting substantially of a porous ceramic insulating layer comprising, in weight percent, zirconia partially stabilized with about 6-8 yttria, wherein the porous ceramic insulating layer has a porosity between about 20-35 volume percent.

19. A method of insulating a metallic substrate consisting substantially of:

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a. providing a clean substrate surface; and
b. depositing a porous ceramic insulating layer comprising, in weight percent, zirconia partially stabilized with about 6-8 yttria and having a porosity between about 20-35 volume percent.

20. An article or method as claimed in claim 18 or 19 wherein the substrate is selected from the group consisting of Ni and Co base superalloys

21. An insulating thermal barrier coating system for a metallic substrate comprising:

a. a metallic bond coat which has received no bond coat adherence heat treatment to form a bond between the metallic bond coat and the metallic substrate to which the metallic bond coat is applied; and
b. a porous ceramic insulating layer made of material selected from the group consisting of zirconia stabilized with yttria, zirconia stabilized with ceria, and ceria, wherein porosity is intentionally created within the insulating layer by incorporating a polyester material.

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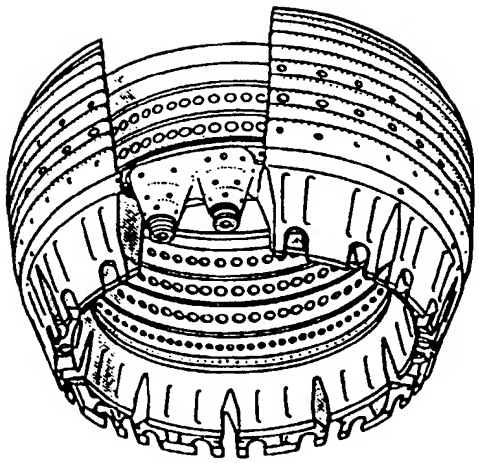

FIG.1

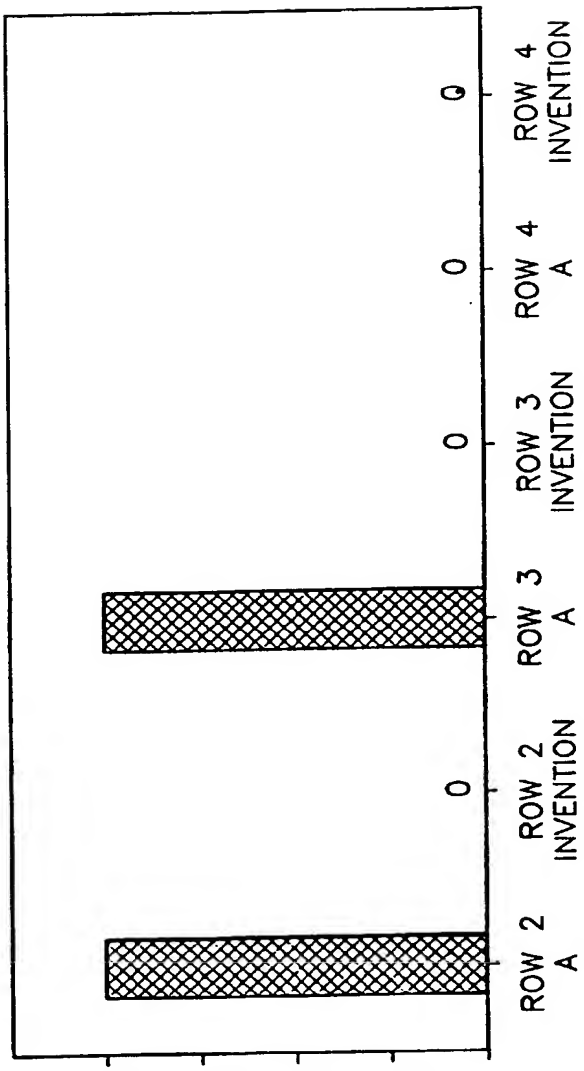

FIG.2

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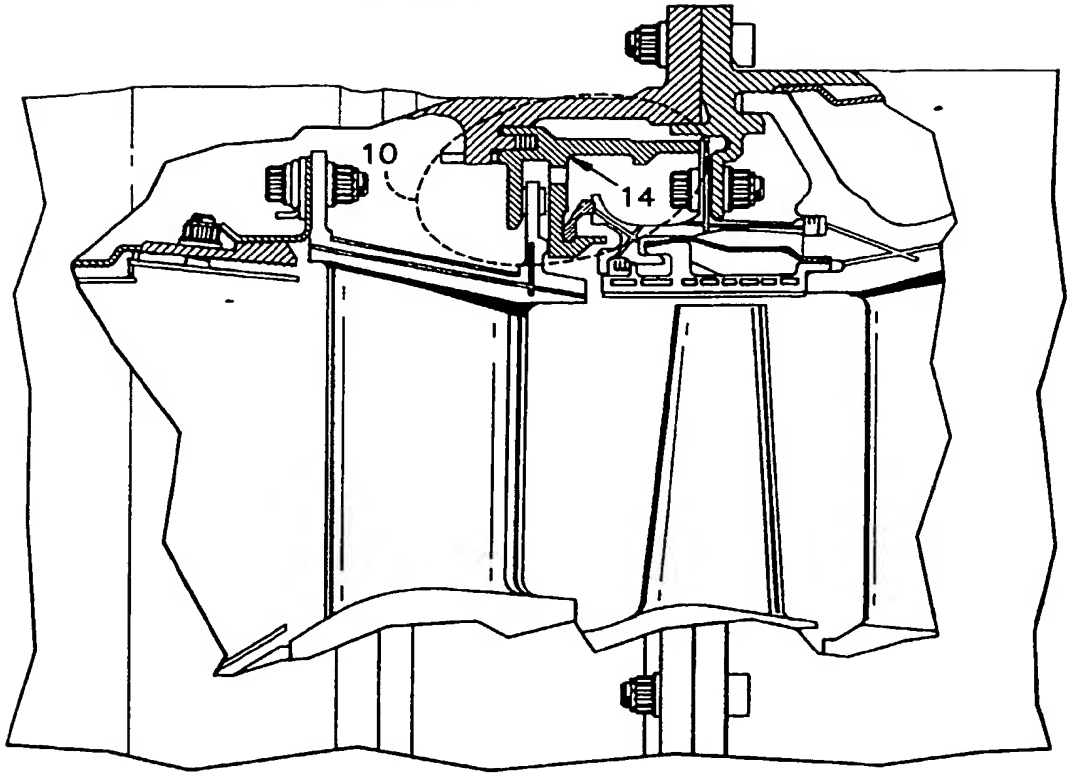
FIG.3



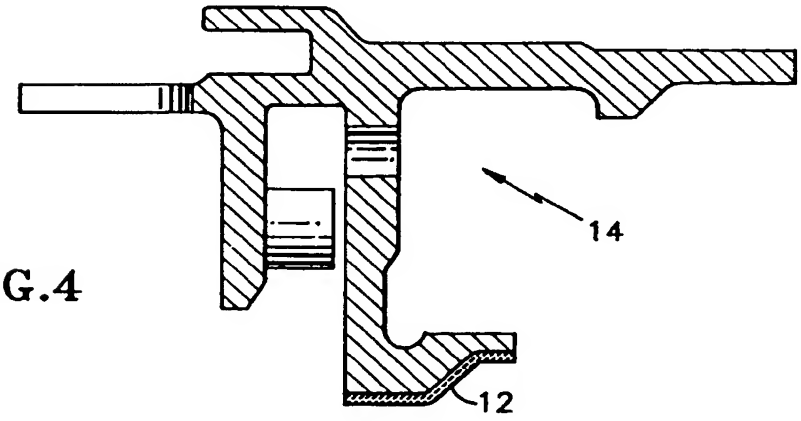


FIG.4

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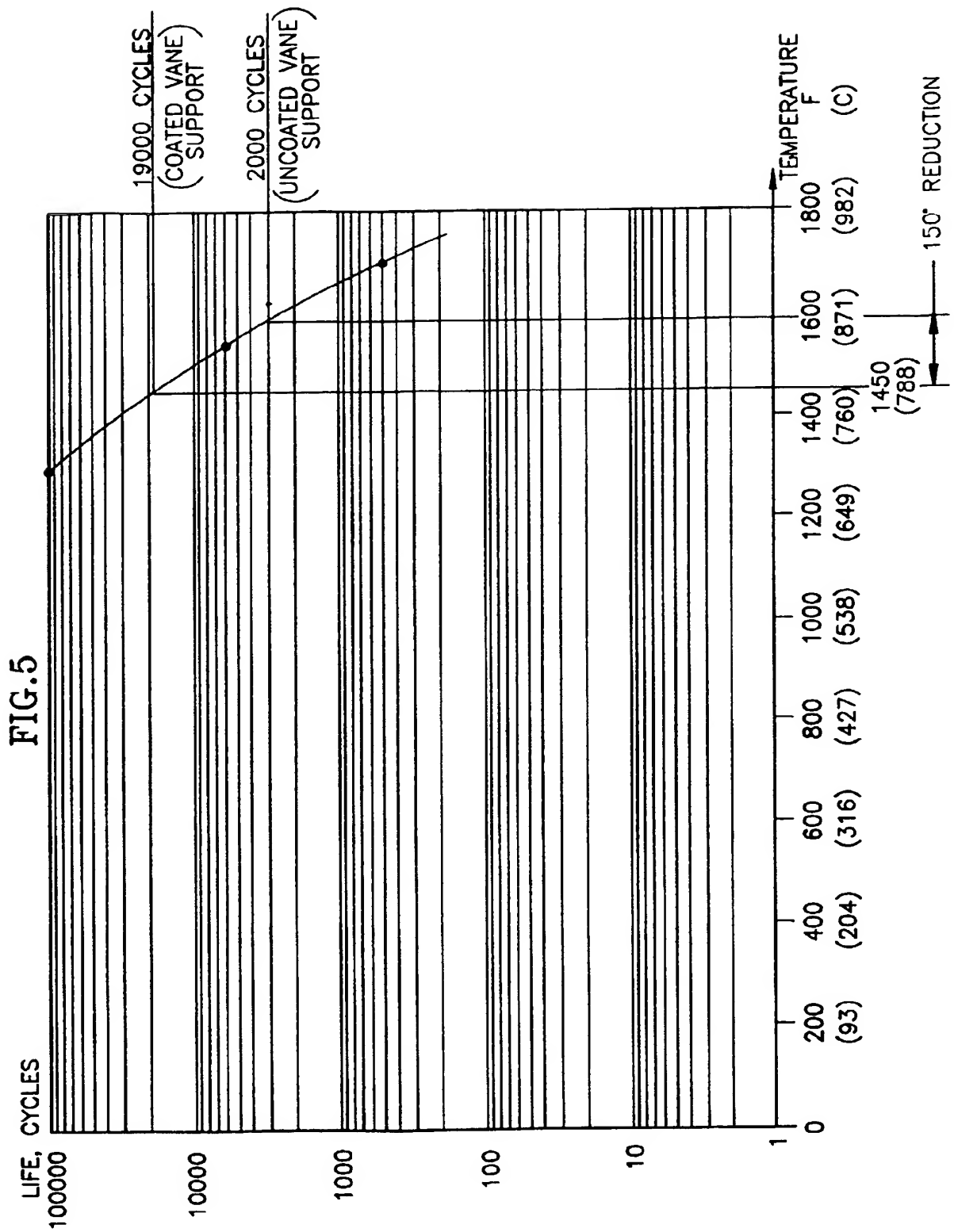

FIG.5

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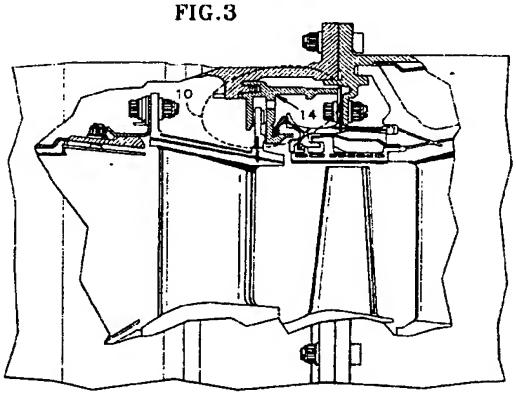
(54) Insulating thermal barrier coating system

(57) The invention concerns a thermal barrier coating system (12) requiring no bond coat adherence high temperature heat treatment and having enhanced insulating capabilities such that it may be applied to gas turbine engine components of varied shape, thickness and size. In preferred embodiments, the system includes a metallic bond coat which does not require a bond coat adherence high temperature heat treatment to form a bond between the metallic bond coat and a metallic substrate to which it is applied. A porous ceramic insulating layer is deposited on the metallic bond coat. In another preferred embodiment, the porous ceramic insulating layer is deposited directly on the metallic substrate.

The coating system is particularly advantageous for insulating metallic components prone to distortion in heat treatment and those requiring insulation in an as machined condition.

FIG.3



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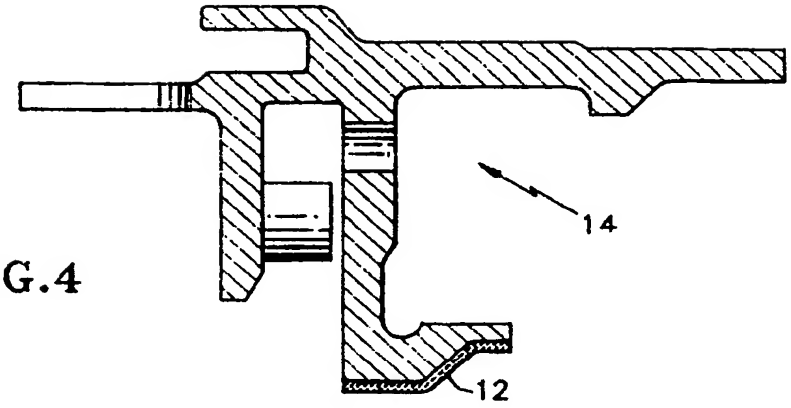

FIG.4

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Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT

EP 97304676.6

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 6)
X	EP 0266299 A2 (UNITED TECHNOLOGIES CORPORATION) 04 May 1988 (04.05.88), the whole document. --	1-21	C 23 C 4/04
X	WO 95/12004 A1 (UNITED TECHNOLOGIES CORPORATION) 04 May 1995 (04.05.95), the whole document. --	1-21	
X	US 5350599 A (RIGNEY et al.) 27 September 1994 (27.09.94), claims, column 4, line 42 - column 5, line 16. --	1,3,9, 16-21	
X	US 4248940 A (GOWARD et al.) 03 February 1981 (03.02.81), the whole document. --	1,2,3, 9,16-21	TECHNICAL FIELDS SEARCHED (Int. Cl. 6)
A	US 4503130 A (BOSSHART et al.) 05 March 1985 (05.03.85), the whole document. ----	1-21	C 23 C B 32 B B 05 D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	01-10-1997	BECK

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